

COMPARATIVE STUDY OF EFFICIENCY OF HETEROPOLY ACIDS INTERCALATED BENTONITE

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ABSTRACT

Heteropoly acids are very efficient catalysts. Combining the efficiency of heteropoly acids and clay we have performed various reactions. Heteropoly acid intercalated clay (Bentonite) proved to be the most efficient catalyst in organic reactions. In this work we have compared the efficiency of different Heteropoly acid intercalated Bentonites and Phosphotungstic acid intercalated Bentonite proved to be the most efficient catalyst.

KEYWORDS: Bentonite, Heteropoly Acid, Organic Reactions, Intercalation

INTRODUCTION

Catalysis by heteropoly acids (HPAs) and related compounds is a field of growing importance, attracting increasing attention worldwide. Heterogeneous acid catalysis by heteropoly acids (HPAs) has the potential of substantial economic and green benefits. A **heteropoly acid** is a class of acid made up of a particular combination of hydrogen and oxygen with certain metals and non-metals. This type of acid is a common re-usable acid catalyst in chemical reactions. Keggin HPAs, have general formula $X_{n+}M_{12}O_{40}^{n-8}$, where X is the central atom (Si^{+4} , Ge^{4+} , P^{5+} , As^{5+} , etc.), n the degree of its oxidation, and M is molybdenum or tungsten, which can be partly replaced by other metals [1]. The structure of Keggin compounds, comprises four trigonal groups of edge-sharing MO_6 octahedra, each group sharing corners with neighboring groups and with the central tetrahedron (α -structure).

In each octahedron the metal is displaced towards the terminal oxygen atoms. This structural arrangement leads to the formation of a spherical polyanion. Heteropoly acids, their salts and supports are known to be active catalysts for many homogeneous and heterogeneous acid catalyzed reactions [2-4]. The reason why heteropoly catalysts are attractive is their variety and high potential as catalyst. Being stronger acids, HPAs have significantly higher catalytic activity than mineral acids. This makes it possible to carry out the catalytic process at a lower catalyst concentration and/or at a lower temperature. Further, heteropoly acid catalysis lacks side reactions.

As stable, relatively nontoxic crystalline substances, HPAs are also preferable with regard to safety and ease of handling. Its application, however, has been limited because of the difficulty of catalyst regeneration due to a relatively low thermal stability of HPAs. These limitations can be overcome by combining the HPA with Clays. Clays are molecularly engineered aluminium/magnesium silicates having 1:1 or 2:1 layer structures. Natural clays possess various uses and applications. Most of the acid catalysed reactions can be done using clay as a catalyst. Clay catalyses a wide variety of reactions [5-8]. But the acidity of natural clay is very low which can further be enhanced by intercalating clay with HPA. We have synthesized different HPA intercalated clay which proved to be very efficient catalyst [9-11]. We have compared the efficiency of different HPA intercalated clays.

EXPERIMENTAL

Catalyst Preparation

The different heteropoly acid intercalated Bentonites (HPA-Ben) such as Phosphomolybdic acid intercalated Bentonite (PMA-Ben), Silicotungstic acid intercalated Bentonite (STA-Ben), Phosphotungstic acid intercalated Bentonite (PTA-Ben) has been synthesized.

Comparative Study of Efficiency of HPA-Ben

Three series of reactions, deoxygenation of Oximes, synthesis of acetal derivatives of aldehydes and ketones and synthesis of coumarin derivatives have been performed using Bentonite, heteropoly acids (HPA) and HPA intercalated Bentonites (HPA-Ben) as catalyst [9-11]. From the above series of reactions it has been proved that the HPA-Ben is a better catalyst [9-11]. The comparative study of the catalytic activity of PMA-Ben, STA-Ben and PTA-Ben has been done. The reactions (showing highest and lowest yields) [9] from the above series (deoxygenation of Oximes, synthesis of acetal derivatives of aldehydes and ketones) have been selected and catalytic activity of PMA-Ben, STA-Ben and PTA-Ben has been checked using the selected reactions.

Comparative study of the catalytic activity using deoxygenation reaction has been shown in the table 1

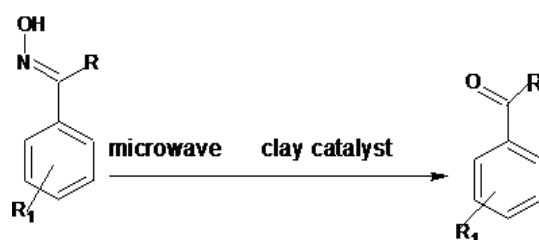


Figure 1

Table 1: Efficiency of Reaction as a Function of Catalyst (HPA & HPA-Ben)

R	R ₁	Time, Sec	% Yield with Various Catalysts					
			PMA	STA	PTA	PMA-Ben	STA-Ben	PTA-Ben
H	p-OCH ₃	40	85	88	92	98	98	98
H	o-Cl	80	70	74	80	87	90	94

From the second series i.e. synthesis of acetal derivative of aldehydes and ketones, the synthesis of acetal derivative of 4-bromo Acetophenone was selected for comparative study of the catalytic activity [11]. The reaction was selected because of having the lowest yield. The results are shown in the table 2

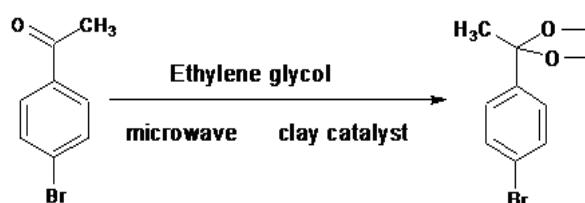


Figure 2

Table 2: Efficiency of Reaction as a Function of Catalyst (HPA & HPA-Ben)

Time, Sec.	%Yield with Various Catalysts					
	PMA	STA	PTA	PMA-Ben	STA-Ben	PTA-Ben
300	60	63	67	72	75	<u>80</u>

From the third series i.e. synthesis of coumarin derivative, the synthesis of 7, 8-benzo-4-methyl coumarin was selected for comparative study of the catalytic activity. The reaction was selected because of having the lowest yield [10]. The results are shown in the table 3

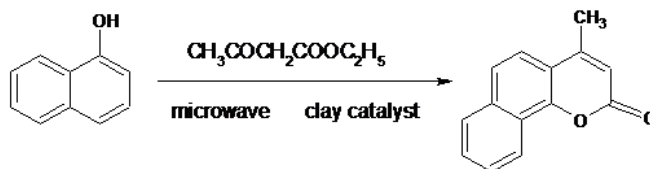


Figure 3

Table 3: Efficiency of Reaction as a Function of Catalyst (HPA & HPA-Ben)

Time, Sec	%Yield with Various Catalysts					
	PMA	STA	PTA	PMA-Ben	STA-Ben	PTA-Ben
420	56	60	65	70	74	78

RESULTS AND DISCUSSIONS

It has been found that for the same reaction the results obtained with PTA-Ben are better (yield is more) as compared to PMA-Ben and STA-Ben. It has also been shown that for the deoxygenation of p-anisaldehyde the yield is 99% with PMA-Ben. So, there is not much scope of increase in yield. The yield with STA-Ben and PTA-Ben has also been found to be 99%. For the deoxygenation of p-bromo Acetophenone the yield has increased upto 5% with STA-Ben and another increase of 5% has been observed with PTA-Ben.

From the comparative study of all the three series of reactions it has been concluded that PTA-Ben is the most efficient catalyst.

Spectral Studies of the Products Prepared

The products synthesized during the different reactions have been characterized using FT-IR and NMR spectroscopy techniques.

2-Chloro Benzaldehyde: IR (ν in cm^{-1}) 3100 (aromatic C-H), 1592,1568,1443 (aromatic ring), 1698 (C=O), 756 (o-Subs.); ^1H NMR δ 10.2 (s,1H, CHO), 7.6 (d, 1H, H 3 Aromatic), 7.8 (d, 1H, H 6 Aromatic), 7.4-7.5 (m, 2H, H 4,5Aromatic).

4-Methoxy Benzaldehyde: IR (ν in cm^{-1}) 3010 (aromatic C-H), 1579,1511,1461 (aromatic ring), 1685 (C=O),1261 (C-O), 833 (p-Subs.); ^1H NMR δ 9.8 (s,1H, CHO), 7.8 (d, 2H, H 3,5 Aromatic), 7.5 (d, 2H, H 2,6 Aromatic), 3.8 (s,3H,OCH₃).

4-Bromo Acetophenone Acetal: IR (ν in cm^{-1}) 3107 (aromatic C-H), 1598, 1498 (aromatic ring), 1027 (C-O), 824 (p-Subs.), 628 (C-Br); ^1H NMR δ 7.5 (d, 2H, H_{2,6} Aromatic), 7.1 (d, 2H, H_{3,5} Aromatic), 4.3 (t, 2H, CH₂), 4.2 (t, 2H, CH₂), 2.3 (s, 3H, CH₃).

7,8-Benzo-4-Methylcoumarin: IR (ν in cm^{-1}) 1593, 1576, 1474 (aromatic ring), 1632 (C=O), 1278, 1084 (C-O); ^1H NMR δ 8.5 (d, 1H, H Aromatic), 7.8 (d, 1H, H Aromatic), 7.5-7.6 (m, 2H, H Aromatic), 7.4 (d, 1H, H aromatic), 6.9 (d, 1H, H aromatic), 6.4 (s, 1H, H 3 Aromatic), 2.5 (s, 3H, CH₃).

REFERENCES

1. Kozhevnikov, I.V. (1987). Advances in Catalysis by Heteropolyacids. Russ.Chem. Rev, 56(9), 811-825

2. Kozhevnikov, I.V. (1995). Heteropoly Acids and Related Compounds as Catalysts for Fine Chemical Synthesis. *Catal. Rev. Sci. Eng.*, 37(2), 311-352
3. Kozhevnikov, I.V. (1998). Catalysis by Heteropoly Acids and Multi-component Polyoxometalates in Liquid-Phase Reactions. *Chem. Rev.*, 98, 171-198
4. Mizuno, M., Misono, M. (1998). Heterogeneous Catalysis. *Chem. Rev.*, 98, 199-217
5. Adams, J. M., Clapp, T.V., Clement, D. E. (1983). Catalysis by Montmorillonite. *Clay minerals*, 18, 411-421
6. Kaur, N., Kishore, D. (2012). Montmorillonite: An efficient, heterogeneous and green catalyst for organic synthesis. *Journal of Chemical and Pharmaceutical Research*, 4(2), 991-1015
7. Adams, J. M., Clement, D. E., Graham, S. H. (1983). Reactions of alcohols with alkene over an aluminum-exchanged montmorillonite. *Clays and Clay Minerals*, 31, 2, 129-136
8. Yadav, J. S., Reddy, B. V. S., Eeshwaraiah, B., Srinivas, M. (2004). Montmorillonite KSF clay catalyzed one-pot synthesis of α -aminonitriles *Tetrahedron*, 60, 1767-1771
9. Chaudhary, R., Datta, M. (2013). A solvent free method for deoximation reaction. *International journal of applied, physical and bio chemistry research*, 3, 5, 1-12
10. Chaudhary, R., Datta, M. (2014). Synthesis of coumarin derivatives: a green Process. *Eur. Chem. Bull.*, 3(1), 63-69
11. Chaudhary, R., Datta, M. (2013). Silicotungstic Acid Modified Bentonite: An Efficient Catalyst for Synthesis of Acetal Derivatives of Aldehydes and Ketones. *Journal of Analytical Sciences, Methods and Instrumentation*, 3, 193-201